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SHORT COMMUNICATION

Aqueous synthesis and characterization of Ni, Zn co-doped CdSe QDs

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Abstract Ni, Zn co-doped CdSe quantum dots (QDs) were synthesized by chemical precipitation method through aqueous route. The prepared QDs were characterized by X-ray diffraction (XRD) technique, UV–Vis absorption spectroscopy, photoluminescence (PL) spectroscopy and high resolution transmission electron microscopy (HRTEM). XRD technique results indicate that the prepared samples have a zinc blende cubic phase. From UV–Vis absorption spectroscopy technique, the prepared samples were blue shifted with respect to their bulk counter part due to quantum confinement effect. Among different doping ratios examined, a maximum PL emission intensity was observed for CdSe:Ni(1 %):Zn(1 %) QDs. HRTEM pictures show that the prepared QDs were in spherical shape.

Keywords Quantum dots · Zinc blende cubic phase · Blue shift · Quantum confinement effect

Introduction

In recent years, synthesis and characterization of II–VI semiconductor materials at nano scale has attracted the research community, due to their great potential to examine the basic concepts of quantum mechanics [1, 2] and finding applications in various fields such as solar cells [3–5], lasers [6, 7], LEDs [8–10] and biological labeling [11–13] etc. Among the II–VI semiconductor materials, CdSe is one of the interesting n-type semiconducting materials with direct band gap of 1.74 eV at 300 K [14]. Fluorescence spectrum of CdSe QDs over the visible region can be tuned by varying the particle size [15]. The synthetic routes for CdSe QDs in the literature are principally classified into two ways: organometallic method [16, 17] and aqueous method [18, 19]. In organometallic route, it operates at high temperature and uses organic liquids as solvents which are extremely toxic, expensive and pyrophoric in nature. But the aqueous method is environmentally benign, very economic and uses milder conditions to synthesize CdSe QDs. Using this aqueous method, the energy level of CdSe QDs can be modified just allowing guest elements (Mn, Ni, Co etc.) into the CdSe host material and paves the way for discovering the new class luminescent materials with wide range of potential applications. Doping of these ions into the CdSe host material acts as the trap states for electrons and holes and enables the luminescence. However, presence of two different kinds of ions simultaneously in a host material produces fluorescence which is totally different from the emission due to a single ion and this property is very useful for white light generation [20–22].

In the present work, the Ni, Zn co-doped CdSe QDs were synthesized at moderate temperatures using water as a solvent. The structural, optical and morphological properties of the co-doped CdSe QDs were analyzed and discussed. The photoluminescence study reveals that the actual Ni, Zn co-doping concentrations for CdSe QDs enhance the luminescence property.

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Materials and methods

Materials

Cadmium acetate dihydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$), selenium (Se), sodium sulfite (Na_2SO_3), nickel acetate dihydrate ($Ni(CH_3COO)_2{\cdot}2H_2O$) and zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) were purchased from S D Fine-Chem Limited, India. All reagents were analytically graded and used without further purification. The entire work was carried out using deionized (DI) water.

Synthesis of Ni, Zn co-doped CdSe QDs

0.03 mol sodium sulfite and 5 m mol selenium were dissolved in 100 ml DI water in a 250 ml three neck flask. The solution was refluxed and *deaerated* by nitrogen gas for 6 h at 80 °C; finally, sodium selenosulfate solution is formed.

For Ni, Zn co-doped CdSe, different concentrations of nickel acetate dihydrate and zinc acetate dihydrate (equal mole ratio) were added in cadmium acetate dihydrate solution. To this solution, 100 ml of sodium selenosulfate solution was added drop by drop. The entire solution was stirred and heated at 80 °C for 3 h. At the end of the reaction, precipitated Ni, Zn co-doped CdSe QDs formed. The precipitate was centrifuged and then washed twice with water and ethanol for removing impurities present in it. The synthesized QDs were dried at 100 °C for 3 h in hot air oven. Then the dried QDs were crushed as fine particles using agate mortar for further characterizations like XRD, UV–Vis absorption and photoluminescence spectral studies and HRTEM. For the preparation of undoped CdSe QDs, the same procedure was adopted without addition of nickel acetate dihydrate and zinc acetate dihydrate.

Characterization techniques

The X-ray diffraction pattern of powdered sample was recorded at room temperature using an X-ray diffractometer (X'PERT-PRO, PANalytical, Netherlands) with Cu $K_{\alpha 1}$ (1.54060 Å) and accelerating voltage is 40 kV. The data were collected with a step size of 0.05° and a scan step time of 10.16 s per step in the 2θ range from 10° to 80°. The optical absorption and photoluminescence spectra of co-doped CdSe QDs were recorded using a UV–Vis spectrophotometer (UV 1800, SHIMADZU, Japan) and a fluorescence spectrometer (LS55, Perkin Elmer, USA), respectively. The morphological study was carried out using High Resolution Transmission Electron Microscope (JEOL 3010, JEOL, Japan) with an operating voltage of 300 kV.

Results and discussion

Figure 1 shows the XRD spectra of undoped and Ni, Zn co-doped CdSe QDs. The peak positions of all the prepared samples can be assigned to (111), (220) and (311) diffraction planes of zinc blende cubic phase (JCPDS: 19-0191). XRD patterns reveal that the observed broad peaks due to the synthesized particles are in nano nature. No other peaks belonging to impurity phase were detected; it implies that samples are of high purity. With increasing concentrations of the Ni, Zn doping in CdSe, the spectra remain same, indicating that zinc blende cubic phase is not tailored by the addition of dopants. This may be attributed to the similarity in ionic radius of Ni^{2+} (0.70 nm) and Zn^{2+} (0.74 nm) ions. The average crystallite size is estimated by Debye–Scherrer's formula,

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where k is a constant (about 0.9), $\lambda = 1.54060$ Å (Cu K_{α} radiation wavelength), β is full width at half maximum and θ is the Bragg's diffraction angle. The prepared particles are QDs, because the size of particles is smaller than the Bohr exciton radius of excitons which is 5.6 nm for CdSe [23]. The calculated crystallite size values for undoped CdSe QDs are 4.4 nm and Ni, Zn co-doped CdSe QDs are 4.19, 4.10, 3.88, 3.56 and 3.42 nm, respectively. The decrease in particle size indicates that the dopants can

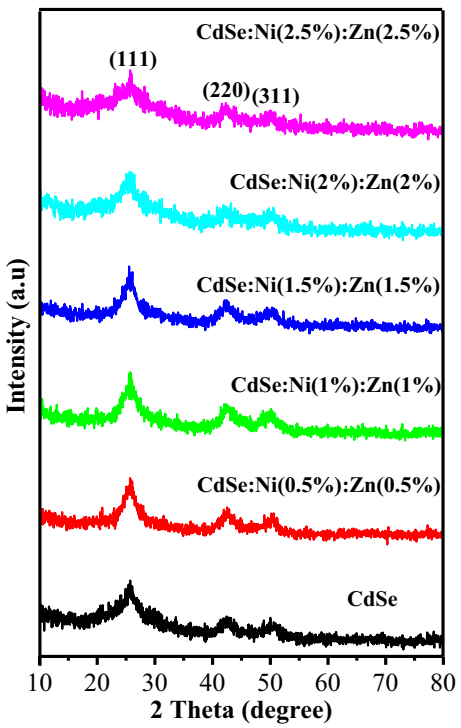

Fig. 1 XRD spectra of undoped and Ni, Zn co-doped CdSe QDs

restrain the agglomeration of CdSe and improve the surface areas of CdSe particles. The calculated lattice constant for undoped CdSe QDs is 6.0630 Å and CdSe:-Ni(1 %):Zn(1 %) is 6.0614 Å. The decrease in lattice constant is due to the replacement of Cd^{2+} ions by Ni^{2+} and Zn^{2+} ions, since the ionic radius of Cd^{2+} (0.92 nm) is greater than the Ni^{2+} (0.70 nm) and Zn^{2+} (0.74 nm). This confirms that the Ni^{2+} and Zn^{2+} ions were incorporated well in Cd^{2+} lattice sites.

UV–visible absorption spectra of undoped and Ni, Zn co-doped CdSe QDs are displayed in Fig. 2. The absorption wavelengths were appeared at 583 nm and 576, 573, 566, 555 and 550 nm for undoped and Ni, Zn co-doped CdSe QDs, respectively, which were significantly blue shifted with respect to the bulk CdSe (716 nm) with a direct band gap of 1.74 eV [24]. It picturises the reduction of the crystallite size in the nanoscale and this shifting is due to the quantum confinement effect [25]. The absorption peak of the co-doped CdSe QDs is shifted toward to the higher energy of the electromagnetic spectrum than the undoped CdSe QDs, when increasing the co-doping concentrations, which clearly indicates that Ni and Zn ions influence on the electronic structure of the CdSe QDs.

The band gap (E_g) of undoped and Ni, Zn co-doped CdSe QDs, shown in Fig. 3, was determined by Tauc's plot of $(\alpha h\nu)^2$ versus $h\nu$ [26]. Where α is an absorption coefficient, which is obtained from the simple relation,

$$\alpha = \frac{2.303A}{l}$$

where A is the absorbance, l is the optical path length of the cell (1 cm) and $h\nu$ is the photon energy. The estimated band gap of undoped CdSe QDs is 2.12 eV and for Ni, Zn co-doped CdSe QDs is 2.16, 2.20, 2.26, 2.28 and 2.33 eV. The increase in band gap values was due to the simultaneous doping of Ni, Zn ions in CdSe host material, this leads to the modification of energy level in co-doped samples.

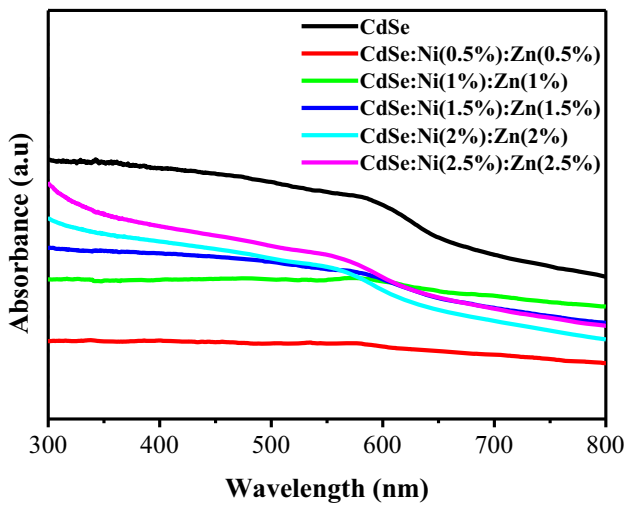

Fig. 2 UV–Vis absorption spectra of undoped and Ni, Zn co-doped CdSe QDs

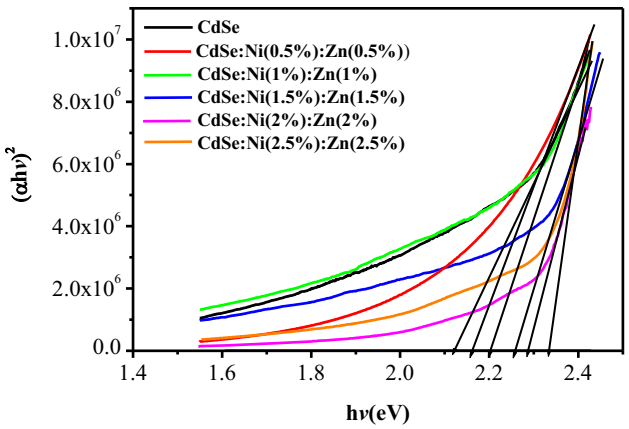

Fig. 3 Tauc's plot for undoped and Ni, Zn co-doped CdSe QDs

The PL spectra of undoped and Ni, Zn co-doped CdSe QDs with different concentrations are shown in Fig. 4. The emission wavelength was located at 603 nm for undoped CdSe QDs and 605, 607, 610, 611 and 614 nm for Ni, Zn co-doped CdSe QDs. The observed PL emission spectrum for CdSe QDs was due to the surface defect states (Cd^{2+} and Se^{2-} ions vacancies) [27]. All the PL spectra of co-doped CdSe QDs were redshifted from those of the undoped CdSe. This might be due to creation of the trap state between the valence and conduction bands by the dopants. Therefore, a little amount of energy is given to the closest lattice sites when the electron switches from the conduction band to the trap state. Moreover, with an increase of doping level, the PL intensity increases to a maximum for CdSe:Ni(1 %):Zn(1 %) QDs. The enhanced luminescence may be explained by the following way: the photons are absorbed by the nanosized CdSe matrix, then

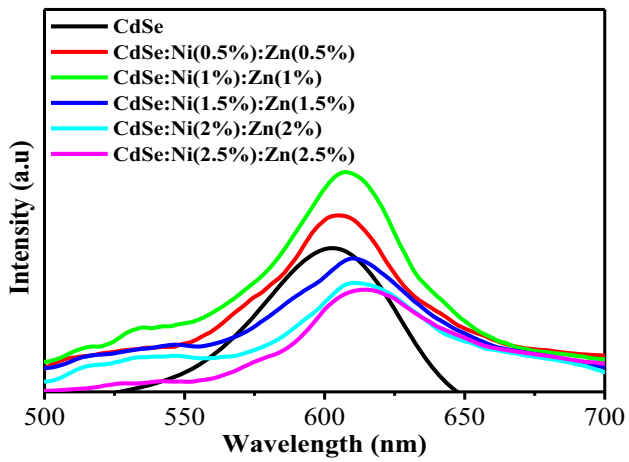

Fig. 4 PL spectra for undoped and Ni, Zn co-doped CdSe QDs

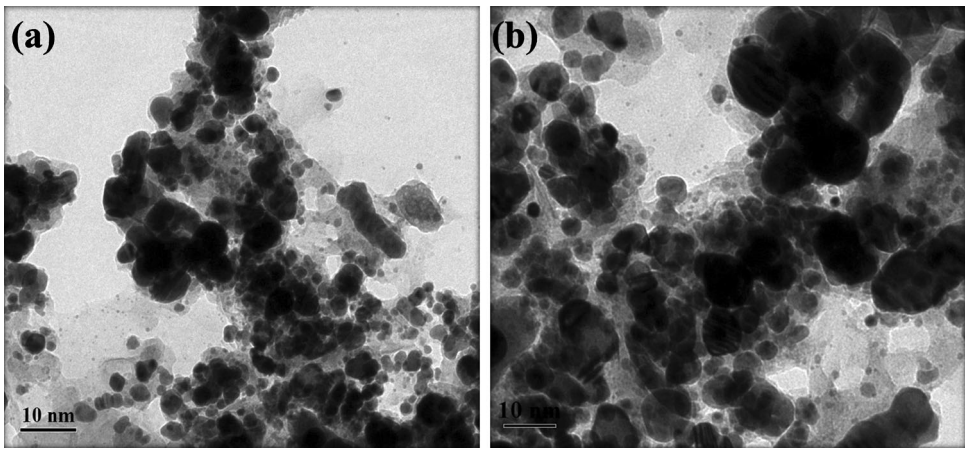

Fig. 5 HRTEM pictures of **a** undoped and **b** Ni(1 %):Zn(1 %) co-doped CdSe QDs

the excited electrons go to the valence band to the conduction band and are trapped by surface defect states. The recombination of surface defect states and the excitation states of Ni^{2+} and Zn^{2+} ions were induced by the occurence of composite centers of Ni^{2+} and Zn^{2+} ions, and the luminescence was observed. In addition, the PL intensity of the co-doped QDs was reduced by increase in the Ni, Zn concentrations. This PL quenching may be due to increase in the radiationless transition by higher concentrations of Ni and Zn ions.

HRTEM images of the undoped CdSe QDs and Ni, Zn co-doped QDs are shown in Fig. 5a, b. It reveals that the both samples (undoped and co-doped) were in spherical shape and aggregated due to the surface energy of QDs. The average particle size of the undoped and Ni, Zn co-doped CdSe QDs was 4.4 and 4.2 nm, respectively, and it is consistent with size calculated by XRD analysis.

Conclusion

The Ni, Zn co-doped CdSe QDs were synthesized by simple chemical precipitation method via aqueous medium. XRD analysis exhibits that the prepared QDs were in zinc blende cubic phase and their sizes estimated to be in the range of 4.4–3.4 nm. The UV–Vis absorption studies show that the absorption peak of the co-doped CdSe QDs is strongly blue shifted with respect to their bulk CdSe due to the quantum confinement effect. From PL studies, the highest luminescence intensity was observed at 607 nm for CdSe:-Ni(1 %):Zn(1 %) QDs. The shape of the prepared co-doped CdSe QDs was in spherical shape, and it was confirmed by HRTEM analysis. Hence, the results suggest that the co-doped QDs could find applications in optoelectronic devices.

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